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COMPLETE SPECIFICATION

Water-Proofing of Fabrics

We, WINGFOOT CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, with offices at 1144, East Market Street, Akron, Ohio, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to new coated fabrics capable of transmitting water vapor. More specifically, the invention relates to water-impermeable, water-vapor-permeable fabrics having a coating of natural or synthetic rubber.

The application of water-proof coatings to cloth is well known and many satisfactory methods have been devised for effecting this objective. However, when the cloth, thus treated is to be used for garments such as raincoats, these coating compositions are not wholly satisfactory because they do not transmit the water vapor resulting from body perspiration. As a result, the comfort of the wearer is greatly impaired. To overcome this objection, light-weight fabrics of closely woven fibers are widely used for the manufacture of so-called rain-proof garments because they do transmit water vapor, but these fabrics are not sufficiently water-proof to prevent the penetration of liquid water when subjected to rainfall for long periods of time or to substantial hydrostatic pressure. Rain-proof garments have also been made by treating woven fabrics with organic silicon compounds, such as the silanes, or other compounds which render the fabric hydrophobic, or water-repellent, but these also do not withhold water under the hydrostatic pressures experienced in normal usage.

The primary purpose of this invention is to provide new water-proof fabrics

capable of excluding liquid water under substantial hydrostatic pressures and yet which are quite pervious to gases, and especially to water vapor.

In accordance with this invention woven fabrics may be coated, with specially compounded natural or synthetic rubbers. Useful rubbers are the polydiene rubbers, such as polyisoprene, polymerized butadiene-1,3, polymers of other conjugated diolefinic hydrocarbons, and the polymers of chlorine-substituted diolefinic hydrocarbons, for example, 2-chloro-butadiene-1,3, natural rubber, the butadiene copolymers, synthetic rubbers, such as the copolymers of 40 to 80 per cent. of butadiene-1,3 or isoprene and 20 to 60 per cent. of a polymerizable mono-olefinic compound, and the butyl rubbers, which are copolymers of 0.25 to 10 per cent. of a conjugated diolefinic hydrocarbon, such as butadiene-1,3 and isoprene, and from 90 to 99.75 per cent. of an iso-olefine, such as isobutylene. The coating of cloth with these rubbers is not new and such practice will not, of itself, yield a water vapor pervious fabric.

In order to secure the desired result, the coating compositions are specially compounded with large proportions of a hydrophilic diatomaceous earth or other similar naturally occurring fossil remains of microscopic marine animals, including diatoms and other protophyta. These minerals are known as infusorial earth, diatomaceous silica, and kieselguhr and are available in various states of refinement under the trade names of "Sil-o-cel," "Celite" (Registered Trade Marks) and "Superfloss." For the purpose of this patent application all of these minerals in their natural state and in purified form are intended to be included within the generic expression "diatomaceous earth."

[Price]

The different minerals vary substantially in their densities and for the purpose of defining the invention it has been found that the volume ratios of the diatomaceous earth are more significant than the weight ratios. The coating compositions used in the invention are prepared by compounding the natural or synthetic rubber with at least two volumes of diatomaceous earth, the volume being based on the so-called "apparent density" measured by pouring the pigment into a graduate or other volume measuring device. The preferred compositions will contain from three to five volumes of diatomaceous earth. If more than six volumes of the pigment are used, many compositions become too rigid or viscous for ready application to cloth, especially when the latex technique, hereinafter described, is used.

A preferred method for preparing the new compositions involves the use of the natural latices or the synthetic latex as it is obtained by the conventional emulsion polymerization techniques. Such latices are aqueous suspensions of finely-divided solid particles of polymer, the synthetic emulsions being usually stabilized by the presence of soap or other wetting agent, and the natural latices being stabilized by means of ammonia or caustic soda. The latex may be used directly in this form, or it may be concentrated by creaming, agglomerating or centrifuging in any manner well known to the art. The solid rubber content of these aqueous suspensions may vary between 30 and 55 percent solids. In the practice of this invention the natural or synthetic latices are compounded with anti-oxidants, accelerators, plasticizers and coloring agents in the manner well known to the art. Suitable anti-oxidants are phenyl-beta-naphthylamine, butyraldehyde-aniline derivative and di-beta-naphthyl-para-phenylene diamine. The conventional accelerators used in these compositions are hexamethylene ammonium hexamethylene-dithio-carbamate, potassium salt of mercapto-benzothiazole, zinc oxide, and magnesia and litharge. To improve the visual appearance colored pigments and dyes may also be incorporated. In addition to the conventional modifying agents, the diatomaceous earth is added in the amounts specified above. When so compounded the latex is a viscous liquid or a semi-solid paste.

Other very effective coating compositions may be prepared by compounding solid natural or synthetic rubber on a rubber mill with the conventional anti-oxidants, plasticizers, and accelerators, as above described. The rubber so com-

pounded is then dissolved or dispersed in organic solvents, such as benzene, toluene, methyl ethyl ketone, ethylene dichloride, chlorobenzene, and high naphthenic petroleum fractions. Although sometimes regarded as true solutions, the mixtures of organic solvents and natural or synthetic rubbers are believed to be colloidal dispersions of rubber particles in the organic liquids in which the organic liquid is the exterior phase, or dispersion medium, just as the water is the exterior phase of a latex, or aqueous dispersion. The dispersion of the natural or synthetic rubber in the solvent is effected by adding the compounded rubber to the solvent in a dough mixer or other conventional mixing device. Sufficient solvent is added to make a thin cement and the desired amount of the diatomaceous earth is thereafter added to yield a thick cement which can be fabricated by the same methods useful in the fabrication of the compounded latex, by painting, spraying, calendering, spreading or other methods well known to the art.

The principal use of the above-described coating compositions is in the coating of fabrics which may be woven or knitted of animal fibre, such as wool, silk, fur and hair, vegetable fibre, such as cotton, linen and hemp, mineral fibre, such as glass and asbestos, and synthetic fibre, such as rayon or nylon. Matted fabrics, such as felt and paper may also be coated. The apparatus and method used for impregnating or coating the fabrics are well known and are not a part of this invention.

The preferred method of applying the coatings involves the "spreading" technique, in which cloth is drawn tightly over a series of rolls or other devices and the compounded latex or solvent dispersion is applied using a doctor blade or other straight edge to control the thickness. The blade may be set up perpendicularly to the fabric or at an angle so as to force the coating composition into the interstices. Frequently it is desirable to apply several successive layers, allowing each to dry wholly or partially before applying the next layer. The first layer is sometimes applied with the spreader knife set at zero clearance so that only the interstices are filled on the first application, the desired covering layers being put on subsequently by separate spreading operations. After each coating, or after several coatings have been applied, the composition is dried, by heating, if necessary, to remove the water or other liquid present in the rubber dispersion. The dried coating is then vulcanized by heating the coated fabric

to the vulcanization temperature of the particular compound.

The coated fabrics may be used in the fabrication of coats, gloves, boots and shoes, and other wearing apparel as well as tents, sleeping bags, hospital sheeting, bandage wrappers, tarpaulins, furniture coverings or other structures adapted for enclosing or contacting the human body.

- 10 The water vapor perviousness of the coated fabrics may be tested by any of several standard methods. In the examples below the coated fabrics were tested by cementing a sample of the fabric 15 to the top edge of a glass Petri dish containing water, the level of which is 2.3+.05 cm. below the fabric, and measuring the water evaporated during a predetermined period of time. The water vapor transmitted, which is expressed in grams per hour per square meter, is corrected for variations in temperature and humidity by running a control with a standard balloon cloth (Sak or pima 20 cotton, 2.0+.1 oz./yd.², warp count 133, fill count 134, plain weave) and multiplying the measured moisture vapor transmission of the test sample by 47.5, the average moisture vapor transmission of the 25 standard cloth, and dividing by the control measurement of the standard cloth. This method of testing gives accurate reproducible test data. Conventional fabrics water-proofed by rubber coatings 30 usually have moisture vapor transmissions of less than 5 grams per hour per square meter, while fabrics prepared in accordance with this invention will have moisture vapor transmissions in excess of 40 15 grams per hour per square meter and preferably in excess of 20 grams per hour per square meter.

The hydrostatic head of a film or fabric is the pressure, usually measured in 45 height of water, which is required to force water through the film or fabric. The hydrostatic head may be measured by the method, ASTM D583—40T, Procedure B, Section 6. Water-proof fabrics should 50 have hydrostatic heads of over 125 cm. of water and preferably over 200 cm. of water, whereas the hydrostatic heads of water-repellent fabrics do not exceed 75 cm. of water.

- 55 Although fabrics have been prepared with hydrostatic heads within the above defined preferred range, it has been accomplished by sacrifice of the moisture vapor transmission rate. Similarly 60 fabrics of the desired vapor transmission rates have been prepared but only by giving up the desirable resistance to liquid water under pressure. This invention makes it possible to achieve both of 65 the desired properties to an effective

extent.

Further details of the preparation of the coating compositions and the laminated fabrics prepared therefrom are set forth with respect to the following specific 70 examples.

EXAMPLE 1.

A polychloroprene latex containing approximately 50 per cent. rubber solids (Neoprene 571) was mixed with the 75 following materials, the quantities being based on 100 parts by weight of the polychloroprene:

Casein	- - - - -	5	
Water glass	- - - - -	15	80
Calcium carbonate	- - - - -	25	
Zinc oxide	- - - - -	25	
Hexamethylene tetramine	- - - - -	3	
*Agerite White	- - - - -	3	
Methyl cellulose	- - - - -	3	86

*Antioxidant sym. dibetanaphthyl-p-phenylene diamine.

The casein was added as a 10 per cent. water solution of ammonium caseinate and the water glass was also added in 90 water solution. The materials were mixed by means of high speed propeller type agitators, and, when thoroughly mixed, 90 parts of water were added. One hundred parts by weight (3.5 volumes) of 95 diatomaceous silica were then thoroughly mixed into the latex.

The latex paste so prepared was spread on cotton sheeting weighing 3.6 oz./sq. yd. and having 58 threads per inch in 100 the warp and 50 threads in the fill. The fabric was coated with three layers of the material and with spreading knife set at 0.001—0.002 inch. Each layer was dried thoroughly over steam coils before applying the next layer. The coated fabric was cured in an oven for 50 minutes at 105° C. The resulting product was measured to determine its moisture vapor transmission which was found to be 22 grams/hr./m². 110 The hydrostatic head was measured and found to be 200 cm. of water.

EXAMPLE 2.

A polychloroprene rubber (GR—M) was milled on a laboratory-size rubber mill 115 with the following materials; the parts being by weight based on 100 parts of polychloroprene:

Zinc oxide	- - - - -	10	
Calcined magnesia	- - - - -	10	120
Phenylbetanaphthylamine	- - - - -	2	
Sulfur	- - - - -	2	

The compounded rubber was placed in a dough mixer and thinned by 762 parts by weight of toluene. After mixing to a thin 125

uniform cement 112 parts by weight (4 volumes) of diatomaceous silica were added.

After this, the cement was spread on a cloth fabric identical to that used in the preceding example by coating once with the doctor blades and thereafter with three coats each 0.001 to 0.002 inch in thickness. The coated fabric was then dried in hot air to evaporate the excess toluene and cured for 60 minutes at 280° F. The hydrostatic head was found to be 287 cm. of water and the moisture vapor transmission was found to be 35 grams./hr./m².

EXAMPLE 3.

A synthetic rubber copolymer of approximately 72 per cent. of butadiene-1,3 and 28 per cent. of styrene was compounded with the following materials, the quantities being based on 100 parts by weight of the copolymer.

	Stearic acid	- - - - -	1.00
	Phenyl-beta-naphthylamine	- - - - -	2.00
25	Zinc oxide	- - - - -	3.00
	Sulfur	- - - - -	1.00
	Mercaptobenzothiazyl disulfide	- - - - -	2.00
	Mercaptobenzothiazole	- - - - -	0.75
	Beta-naphthylamine	- - - - -	1.00

30 The above ingredients were mixed on a roll mill and, after a uniform composition had been obtained, it was placed in a standard dough mixer and sufficient high test gasoline was added to produce a dispersion of approximately 20 per cent. solids. Diatomaceous earth was then added in the amount of 182 parts by weight, based on 100 parts of the copolymer. This was equivalent to 4.8 volumes of diatomaceous earth to one volume of copolymer. Additional gasoline was then added to the solvent dispersion to reduce the solid content to 23 per cent.

45 A cotton sheeting, 3.6 ounces per square yard in weight and 54 × 58 thread count, was coated with the cement by applying the first coat with the spreader knife set at zero clearance and three additional 50 coats each 0.003 inch in thickness. After drying the coated cloth in air, it was cured by heating in a closed oven for 90 minutes at 270° F. The resulting fabric was found to have a hydrostatic head in excess of 300 centimeters of water and a moisture vapor transmission rate of 33 gms./hr./m².

EXAMPLE 4.

55 A copolymer of 70 per cent. butadiene and 30 per cent. acrylonitrile was compounded with the following materials on a standard roll mill, the quantities being based on 100 parts by weight of the copolymer.

Zinc oxide	- - - - -	3.00	65
Sulfur	- - - - -	2.00	
Stearic acid	- - - - -	0.20	
Mercaptobenzothiazole disulfide	- - - - -	0.75	

After the synthetic rubber had been milled to a homogeneous mixture, it was placed in a dough mixer and mixed with methyl ethyl ketone to approximately 20 per cent. solids. Diatomaceous earth was then added to the extent of 142 parts by weight (4 volumes per volume of synthetic rubber). The solvent dispersion was then diluted to 22 per cent. solids by the addition of more methyl ethyl ketone.

Cotton sheeting identical with that used in the preceding experiment was spread with the synthetic rubber cement with the spreading knife set at zero clearance. The fabric so treated was then doubled upon itself with the coating on the outside, and then a layer of the cement 0.01 inches in thickness was applied between the two layers of cloth, thereby laminating a double layer of cloth. After drying, the fabric so treated was cured by heating for 40 minutes at 305° F. in a closed oven. The composition so prepared was found to have a hydrostatic head of 240 centimeters of water and a moisture vapor transmission of 41 gms./hr./m².

EXAMPLE 5.

The following materials were mixed in an open vessel with vigorous mechanical agitation:—

A 2 per cent. methyl cellulose aqueous solution containing 8.2 parts by weight of methyl cellulose and 410 parts of water.

Parts by weight		
Diatomaceous earth	- - - - -	179
Water	- - - - -	361

Each of the following compounding materials, which are readily available commercially as aqueous dispersions containing small amounts of stabilizing agents, were then added (parts by weight of active material):—

Sulfur	- - - - -	2.00	
Zinc oxide	- - - - -	1.50	
Zinc diethyldithio-carbamate	- - - - -	1.00	115
Sym. dibutanaphthyl-p-phenylene diamine	- - - - -	2.00	

After the reagent dispersions were thoroughly mixed, the vigorous agitation was stopped and 170 parts by weight of a commercial Butadiene-Styrene (60:40) copolymer latex containing 58 per cent. solids was gradually added while stirring

slowly to form a thick latex of pasty consistency. This contained 4.8 volumes of diatomaceous earth per volume of copolymer.

- 5 Cotton sheeting identical to that used in Examples 1 and 3 was spread with three tight-gauged coats of the paste and then doubled over and laminated by contacting the spread surfaces. The composition so prepared was dried for 19 minutes at 70° C. in an air oven then cured by heating at 105° C. for 30 minutes. The composition so prepared had a hydrostatic head of 290 centimeters of water and a moisture 15 vapor transmission of 19 gms./hr./m².

EXAMPLE 6.

The following materials were thoroughly mixed on a roll mill:—

	Pounds
20 Natural rubber	32.4
ZnO	1.8
Sulfur	.49
Mercaptobenzothiazole	.66

The milled compound was then added 25 gradually to 95.69 gallons of petroleum naphtha in a standard dough mixer and dispersed therein to form a rubber cement.

A separate benzol solution was prepared by mixing the following materials:—

	Pounds	Gallons
Diethylamine	11.25	
CS ₂	9.2	
Oil Soluble Pigment	.37	
Benzol	97.29	

35 The cloth coating composition was then made by mixing 1900 parts by weight of the rubber cement, 144 parts by weight of diatomaceous earth and then adding to the mixture 56 parts by weight of the 40 benzol solution. This composition contained 3.7 volumes of diatomaceous earth for each volume of rubber.

A balloon cloth weighing two ounces per square yard was spread with the coating composition with the spreader knife set for zero clearance. After drying the initial coat, four additional coats, each 0.005 inch in thickness, were applied, each coating being dried before the next 50 coat was applied. The coated fabric was then cured in air for one hour at a temperature of 270° F. The coating weighed 2.2 ounces per square yard.

The finished fabric was found to have 55 a hydrostatic head in excess of 300 cm. of water and a moisture vapor transmission of 36 gms./hr./m², as compared to 47.5 gms./hr./m² for the uncoated balloon cloth.

EXAMPLE 7.

A natural rubber latex (160 parts by weight) containing 62 per cent. solids was compounded with the following reagents.

	Parts by Wt. 60
Sulfur	1.00
Zinc oxide	1.50
Sym. dibetanaphthyl-p-phenylene diamine	2.00
Zinc diethyldithiocarbamate	.75
Casein (as 10% water solution of ammonium caseinate)	2.00

The reagents were added in the form of aqueous dispersions which contained small amounts of wetting agents or other 75 stabilizers. These dispersions are well known and commercially available rubber compounding reagents. The latex was simultaneously diluted with 25 parts of water (including the water of the dispersion).

A water suspension of diatomaceous earth was then separately prepared by the vigorous agitation of 101.6 parts by weight of diatomaceous earth in a solution of 3.2 85 parts of methyl cellulose in 370 parts of water. The agitator was then slowed down, and 200 parts of the compounded latex were slowly added. The materials were thoroughly mixed while carefully avoiding the beating of air into the latex. This composition contained 4 volumes of diatomaceous earth per volume of rubber.

Cotton sheeting weighing 3.6 oz./yd.² was laminated to itself by passing two 95 layers of the fabric between rolls set with a 0.015 inch clearance. The compounded latex was flowed between the rolls to form an intermediate layer approximately the thickness of the roll clearance. The fabric 100 was then treated for five minutes at 240° F. and cured in air for 60 minutes at 225° F.

This fabric was tested by standard methods and found to have a hydrostatic 105 head of 238 cm. of water and a moisture vapor transmission of 23 gms./hr./m².

EXAMPLE 8.

The following materials were thoroughly mixed on a roll mill, the parts 110 given being by weight:—

	Parts by Wt.
Butyl rubber	100
Stearic acid	2
ZnO	10
Sulfur	2
Mercaptobenzothiazole	4

The compounded rubber was then sus-

- pended in toluene to form approximately a 30 per cent. solids solution, a standard dough mixer being used to effect the dispersion. Diatomaceous silica in the 5 amount of 158 parts by weight was moistened with toluene and then gradually added to the dough mixer which was operated at high speed to achieve a vigorous agitation. After all of the 10 diatomaceous earth had been added, the contained 3 volumes of diatomaceous a 20 per cent. solids suspension. This mixture was diluted with toluene to form earth for each volume of rubber.
- 15 A balloon cloth weighing 2 ozs./yd.² was coated with the cement by spreading it with a rubber bladed knife set at zero clearance. After the initial coating had been dried three additional coats 0.002 20 inch in thickness were applied, drying each coat before the application of the next. The coated fabric was then cured by heating in air at 270° F. for 75 minutes. The resulting coated cloth had 25 a hydrostatic head of 236 cm. of water and a moisture vapor transmission rate of 43 gms./hr./m.² as compared to 47.5 gms./hr./m.² for the uncoated balloon cloth. The coating on the cloth weighed 30 2.29 oz./yd.².
- Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we 35 claim is:—
1. A liquid - water - impervious and water-vapor-permeable fabric which com-
- prises a textile fabric coated with a continuous layer of a natural or synthetic rubber composition deposited from a liquid dispersion of said rubber and from two to six volumes, based on the rubber, of a hydrophilic diatomaceous earth as hereinbefore defined.
2. A coated fabric in accordance with 45 claim 1 in which the rubber is natural rubber.
3. A coated fabric in accordance with claim 1 in which the synthetic rubber is 50 polychloroprene.
4. A coated fabric in accordance with claim 1 in which the synthetic rubber is a copolymer of 40 to 80 per cent. of a conjugated hydrocarbon diene and 20 to 60 per cent. of a polymerizable mono-olefinic 55 compound.
5. A coated fabric in accordance with claim 1 in which the synthetic rubber is a butyl rubber.
6. A coated fabric in accordance with 60 any of claims 1 to 5, inclusive, in which the coating contains from three to five volumes, based on the rubber, of the diatomaceous earth.
7. A coated fabric in accordance with 65 any of claims 1 to 6, inclusive, in which the rubber composition is deposited from an aqueous emulsion.
8. A coated fabric in accordance with any of claims 1 to 6, inclusive, in which 70 the rubber composition is deposited from an organic solvent dispersion.

Dated this 3rd day of June, 1947.

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